

XXV. *Experiments on the Congelation of the Vitriolic Acid.* By James Keir, *Esq. F. R. S.*; communicated by Henry Cavendish, *Esq. F. R. S.*

Read May 3, 1787.

THAT the vitriolic acid sometimes assumes a solid, crystalline state, has been observed by BASIL VALENTINE, and by many later chemists; but their relations of this appearance are neither sufficiently explicit, with regard to the essential and concomitant circumstances, nor do they seem very consistent with each other. It appears, however, that two very distinct species of congelation of this acid have been noticed. That which is described by the older chemists, and also by some modern authors, requires no greater degree of cold than the common temperature of the air, even in summer, and is peculiar to that acid which is obtained by distillation from martial vitriol, and which is possessed of a smoking quality in a high degree: for not only the authors, by whom this congelation has been observed, have given this description of the acid employed, but also the late experiments of M. DOLLFUSS* seem to shew, that the smoking quality is essential to the phenomenon; for neither the acid obtained from vitriol, when deprived by rectification of its smoking quality, nor the English oil of vitriol (which is known to be obtained by burning sulphur, and

* Crell *Annalen* 1785.

which

which does not smoke), were found, by his trials, to be susceptible of this species of congelation. The acid, thus congealed, has been called *glacial*, or *icy oil of vitriol*.

The other kind of congelation has been little noticed till lately. To this congelation every kind of vitriolic acid is subject, whether it smokes or not, and whether it has been prepared from martial vitriol, or from sulphur, provided the cold to which it is exposed be sufficiently intense: for the cold, requisite for this species of congelation, is considerably greater than what is sufficient for the former.

Mr. MACQUER relates, in the second edition of his Dictionary of Chemistry *, that the Duke D'AYEN had observed the congelation of concentrated vitriolic acid, which had been exposed to a cold expressed by 13 or 14 degrees below 0 of REAUMUR's scale; but that mixtures, consisting of one part of the above-mentioned concentrated acid, with two or more parts of water, could not be frozen by the cold to which he exposed them, till he had diluted the acid so much, that its density was to that of water as 104½ to 96; in which latter case of congelation, it is probable, that the water only did freeze, as it does in dilute solutions of neutral salts. M. DE MORVEAU † has made similar experiments, with a view to verify those of the Duke D'AYEN, and with similar success. By means of an intense cold, produced by adding spirit of nitre to pounded ice, he congealed a part of some vitriolic acid, which he had previously concentrated. He observed, that although a very intense cold had been employed to freeze the concentrated acid, it nevertheless remained congealed in much less degrees of cold, and that it thawed very slowly. Lastly, some experiments

* Article, Vitriolic Acid.

† Mem. de l'Acad. de Dijon, pour 1782.

have lately been made by Mr. M^c NAB, at Hudson's Bay, on the congelation of acids by intense cold; an account of which experiments is given in the Philosophical Transactions for 1786, by Mr. CAVENDISH, at whose desire they had been made. These experiments are the more valuable, as the density of the acids employed, and the temperature, and other concomitant circumstances, have been distinctly noted; and they are rendered still more interesting, by the very judicious remarks made on them by Mr. CAVENDISH. It is there related, that a vitriolic acid, whose specific gravity was to that of water as 1843.7 to 1000, froze when exposed to a cold of -15° of FAHRENHEIT's scale; that another more dilute vitriolic acid, consisting of 629 parts of the former concentrated acid, and 351 parts of water, congealed in a temperature of -36° ; and that when the acid was further diluted, it was found capable of sustaining a much greater cold without freezing. In these experiments, as also in those of M. DE MORVEAU, it appeared, that the whole of the acid did not congeal, but that part of it retained its fluidity. Mr. CAVENDISH found, on examining the part which had congealed, and that which had remained fluid, that they were *nearly* of the same strength; and he is thence led to think, that the difference between them, by which the one is more disposed to congeal than the other, does not depend on their different strengths, but on some quality less obvious, and the same which constitutes the difference between glacial and common oil of vitriol. In all the experiments which had been made by the Duke d'AYEN, M. DE MORVEAU, and Mr. M^c NAB, the vitriolic acid, when strong, had frozen with less cold than when diluted; but these experiments did not enable Mr. CAVENDISH to determine, whether this acid has any determinate strength or *point of easiest freezing*

(such as he had discovered to be possessed by spirit of nitre), or whether the cold requisite for congelation does not continually diminish, as the strength of the acid increases, without limitation. This latter opinion he thinks the most probable, from the circumstance of the Duke d'AYEN's and M. DE MORVEAU's acids having frozen with a considerably less intense cold than those of Mr. M^c NAB, which, he supposes, were weaker, as the former acids had been concentrated purposely.

The observations which I have made, and am going to relate, apply solely to the latter kind of congelation of the vitriolic acid, as the acid which I employed was of the kind that is prepared by burning sulphur, and is commonly sold in England under the name of oil of vitriol, and was perfectly free from colour, smell, or smoking quality. After a severe frost at the end of the year 1784, and beginning of 1785, I observed that some vitriolic acid, contained in a corked phial, had congealed; while other parcels of the same acid, some stronger and some weaker, equally exposed to the cold, had remained fluid. As I imputed the congelation to the great intensity of the cold, I was afterwards much surprised, when the frost ceased, to find that the acid remained frozen during many days, when the temperature of the air was sometimes above 40° of FAHRENHEIT's scale; and when the congealed acid was brought into a warm room, purposely to thaw it, a thermometer, placed in contact with it during its thawing, continued stationary at 45°. From these circumstances I concluded, that the freezing and thawing point of this acid was very near the last mentioned degree; and, accordingly, upon exposing the liquor which had been thawed to the air, at the temperature of 30°, the congelation again took place in a few hours. From the circumstance of other parcels of the same acid, but of
different

different strengths, remaining fluid, although they had been exposed to a much greater cold than was necessary for the congelation of that acid liquor which had frozen, I was led to believe, that there must be some certain strength at which the vitriolic acid was more disposed to freeze than at any other, greater or less. I knew that the specific gravity of the acid which had frozen was nearly to that of water as 1800 to 1000, and that of the stronger acid, which had not frozen, was as 1846 to 1000; which last is the usual density of the oil of vitriol commonly sold in England. I knew also, that the acid which had frozen was in no respect but in strength different from the stronger acid which had retained its fluidity; having myself, some weeks before, taken the former acid from the bottle containing the latter, and diluted it with water till it was reduced to the specific gravity of 1800.

Although from the above observations I was convinced of the proposition generally, that the vitriolic acid is most disposed to freeze when at a certain strength, and then it is susceptible of congelation by means of much less cold than has been hitherto imagined; yet, as only part of my acid had frozen, I could not with certainty know the strength of the frozen part, and I therefore was not able to state, with any accuracy, the degree of strength most favourable to congelation, nor the limits of strength within which the acid may be congealed by such moderate cold. In the following winter I had not leisure to pursue the subject; but since the commencement of the present year, I have verified my former observation with more attention to the exact densities of the acids; and I have found, that the point of strength most favourable to congelation is very determinate, and that a very small variation above or below that point renders the acid incapable of freezing without a considerable augmentation of cold. As the

acid, when brought to the proper strength, was capable of freezing with less cold than water does, I immersed several acids of different strengths in melting snow, instead of exposing them to the air, the temperature of which was variable, whereas that of melting snow was constant and determinate. Those acids which would not freeze in melting snow, were afterwards immersed in a mixture of snow, water, and common salt, the temperature of which was not so constant and determinate as that of melting snow; but it generally remained for several hours at about 18° , and was sometimes several degrees lower. The intention of adding water to the snow and salt was to lessen the intensity of the cold of this mixture, and to render it more permanent than if the snow and salt alone were mixed.

The acids which had frozen in melting snow, and which were five in number, having been thawed and brought to the temperature of 60° , were found on examination to have the following specific gravities.

1786

1784

1780

1778

1775

Those acids which would not freeze in melting snow, but which froze when immersed in snow, water, and salt, having been exposed to a greater cold, were of a greater latitude of density. Their specific gravities, when brought to the temperature of 60° , were found to be expressed by the following numbers.

1814

1810

1804

1794

1790

1770

1759

1750

The acids which remained, and which would not freeze either in melting snow, or in the mixture of snow, salt, and water, were found on examination to have the following specific gravities.

1846

1839

1815

1745

1720

1700

1610

1551

It appears, from the first table of specific gravities, that the medium density of the acids which did freeze with the cold of melting snow was 1780; and from the second table it appears, that, at the densities of 1790 and 1770, the acid had been incapable of freezing with that degree of cold. Hence it follows, that 1780 is nearly the strength or density of easiest freezing; and that an increase or diminution of that density, equal to $\frac{1}{178}$ th part, renders the acid incapable of freezing with the cold of melting snow, notwithstanding this cold is some degrees above the freezing point of the most congelable acid. From the second table of specific gravities it appears, that by applying a more intense cold, namely, that produced by a mixture of snow, salt, and water, the limits of the density of the acids capable of congelation were extended to about $\frac{3}{178}$ above or below the point of easiest freezing: and there seems

seems little reason to doubt, that, by greater augmentations of cold, these limits may be further extended; but in what ratio these augmentations and extensions proceed cannot be determined without many observations made in different temperatures.

Although it is probable, that the most concentrated acids may be frozen, provided the cold be sufficiently intense, yet there seems to me reason to believe, that some of the congelations which have been observed in highly concentrated acids have been effected in consequence of the density of these acids having been reduced nearly to the point of easy freezing by their having absorbed moisture from the air: for the Duke D'AYEN and M. DE MORVEAU exposed their acids to the air, in cups or open vessels; and the latter author even acquaints us, that, on examining the specific gravity of the acid which had frozen, he found it to be to that of water as 129 to 74; which density being less than the point of easiest freezing, proves that the acid which he employed, and which he had previously concentrated, had actually been weakened during the experiment. I have several times exposed concentrated oil of vitriol in open vessels in frosty weather; and I have sometimes, but not always, observed a congelation take place. Upon separating the fluid from the congealed part, and upon examining the specific gravity of the latter, after it had thawed, I found that it had been reduced to the standard of easiest freezing. When the congealed acid was kept longer exposed, it gradually thawed, even when the cold of the air increased; the reason of which is not to be imputed to the heat produced by the moisture of the air mixing with the acid, for this cause operated during the congelation, but principally to the diminution of density below the point of easy freezing, which was occasioned by the continued absorption of moisture from the air, and which rendered

rendered the acid incapable of continuing frozen without a great increase of cold.

It appears then, that the concentration of M. DE MORVEAU's acid, at the time of its congelation, from which circumstance Mr. CAVENDISH infers generally, that the vitriolic acid freezes more easily as it is more dense, is not a true premise; and that therefore the inference, though justly deduced, is invalid. On the contrary, there seems every reason to believe, from the analogy of my experiments above mentioned, that as the density of the acid increases beyond the point of easiest freezing, the facility of the congelation diminishes; at least, to as great density as we have been ever able to obtain the vitriolic acid; for if it were possible to divest it intirely of water, it would probably assume a solid state in any temperature of the air.

The crystallization of the frozen vitriolic acid is more or less distinct, according to the slowness of its formation, and other favourable circumstances. Sometimes the crystals are very distinctly shaped, large, and very hard. Their form is the same as the common form of mineral alkali and of selenitic spar, but with angles different in dimensions from either of these. They are solids consisting of ten faces, of which the two largest are equal, parallel, and opposite to each other, and are oblique-angled parallelograms or rhomboids, whose angles are, as near as I could measure them, of 105 and 75 degrees. Between these two rhomboidal faces are placed eight faces of the form of trapeziums. Thus each crystal may be supposed to be composed of two equal and similar frustums of pyramids joined together by their rhomboidal bases. I observed, that the crystals always sunk in the fluid acid to the bottom of the vessel, which shewed that their density was increased by congelation.

I thought

I thought of ascertaining their specific gravity by adding gradually to this fluid part some concentrated vitriolic acid, till the crystals should float in the liquor, the examination of whose specific gravity would determine that of the floating crystals. But I was surpris'd to find, that the crystals sunk even in the concentrated acid, and consequently were denser. I then poured some of the congelable acid, previously brought to the freezing temperature, into a graduated narrow cylindrical glass, up to a certain mark, which indicated a space equal to that occupied by 200 grains of water. The glass was placed in a mixture of snow, salt, and water, and when the acid was frozen, a mark was made on the part of the glass to which the acid had sunk. Having thawed the acid, and emptied the glass, I filled it with water to the mark to which the acid had sunk by freezing, and I found, that fifteen grains more of water were required to raise it to the mark expressing 200 grains; which shews, that the diminution of bulk, sustained by the acid in freezing, had been equal to $\frac{1}{13.3}$ of the whole.

Computing from this *datum*, we should estimate the specific gravity of the congealed acid to have been 1924; but as it contained evidently a great number of bubbles, its real specific gravity must be considerably greater than the above determination, and cannot easily be ascertained on account of these bubbles. By way of comparison, I observed the alteration of bulk which water contained in the same cylindrical glass would suffer by freezing; and I found that its expansion was equal to about $\frac{1}{10}$ th part of its bulk. The water had been previously boiled; but it nevertheless contained numberless bubbles. In this respect then there is a remarkable difference between the congelations of water and of vitriolic acid; but, perhaps, the difference

difference arises principally from the bubbles of elastic fluid, which may be in greater quantity, and may add more to the bulk of the water than of the acid.

Greater cold is produced by mixing snow or pounded ice with the congealed than with the fluid acid, but the quantity I have not determined. There is reason to believe it may be considerable. In the experiments made at Hudson's Bay, by Mr. Mc NAB, the greatest cold which he had produced by mixing acids with snow, was effected by a vitriolic acid which had previously congealed; and to this circumstance of the congelation of the acid, Mr. CAVENDISH justly imputes the intensity of the cold, as the liquefaction of both the frozen acid and the snow had concurred towards this effect; whereas, in mixing fluid acids with snow, the thawing of the snow is probably the sole productive cause.

I was desirous of comparing the times required for the liquefaction of ice and of congealed acid, when both were exposed to the same temperature. For this purpose I filled two equal and similar cylindrical glasses; one with the congelable vitriolic acid, and the other with water; and, after having immersed them in a freezing mixture till both fluids were frozen, and reduced to the temperature of 28° , I withdrew the glasses from the freezing mixture, wiped them dry, and placed them together in a room, where the thermometer stood at 62° . In 40 minutes the ice was thawed, and in 95 minutes the acid was liquefied, at the end of which time the thermometer, which stood near the glasses, had risen to 64° . It appears then, that the congealed acid requires more than twice the time for its liquefaction, when exposed to that temperature, that ice does; but I do not think that we can infer, that the heats absorbed and rendered *latent*, as some late philosophers express them-

felves; or, in other words, that the cold generated by the liquefaction of ice and of congealed acid are in the above proportion of the times, from the following consideration; that, as during the liquefaction of the ice, its temperature remains stationary at 32° , and during the liquefaction of the acid, its temperature remains about 44° or 45° , the ice, being considerably colder than the acid, will take the heat from the contiguous air much faster.

The experiment does however shew, that a considerable quantity of cold is generated by the liquefaction of this acid; and hence it appears probable, that in making experiments of producing cold artificially, by mixing snow with acids in very cold temperatures, it would probably be useful to employ a vitriolic acid of the proper density for congelation, and to freeze it previously to its mixture with snow.

It must not, however, be imagined, that the cold generated by the mixture of these two frozen substances is nearly equal to the sums of the colds generated by the separate liquefactions of the congealed acid and ice, when singly exposed to a thawing temperature: for the mixture resulting from the liquefaction, consisting of the vitriolic acid and the water of the snow, appears, from the generation of heat which occurs in the mixture of these ingredients in a fluid state, to be subject to different laws relatively to heat, than either of the ingredients separately. And the heat, thus generated, as soon as the congealed acid and ice are brought to a fluid state, must counteract, in some measure, the cold produced by the liquefaction.

The vitriolic acid, like water and other fluids, is capable of retaining its fluidity when cooled considerably below its freezing point. I placed a phial, containing some congelable
vitriolic

vitriolic acid, in a mixture of salt, snow, and water; and soon afterwards, while the acid was yet fluid, I immersed in it a thermometer, the mercury of which quickly sunk from 50° to 29° . While I was moving the thermometer in the fluid, in order to make it acquire the exact temperature, I saw the mercury suddenly rise, and upon looking at the acid, I observed numberless small crystals floating in it, which had been suddenly formed. The degree to which the mercury then rose was $46^{\circ}\frac{1}{2}$. Another time, while the acid was freezing, the thermometer placed in it stood at 45° .

From the above observations, the following inferences may be drawn.

1st, That the vitriolic acid has *a point of easiest freezing*; that is, there is a certain strength or density, at which this acid freezes with considerably less cold than at any other strength, greater or less; and that this density is nearly to that of water as 1780 is to 1000.

2dly, That the greater or less disposition of congelation of the vitriolic acid, which is free from the smoking quality that is peculiar to the acid obtained by distilling martial vitriol, does not depend on any other quality or circumstance than its strength or density.

3dly, That the freezing and thawing degree of the most congelable acid is about 45° of FAHRENHEIT's scale. It is, however, to be observed, that this degree is inferred from the temperature indicated by the thermometers immersed in the freezing and thawing acids; but that I never effected the congelation of the fluid acid, without exposing it to a greater cold, namely, either that of melting snow, or of the external air in frosty weather.

Like water, this acid possesses the property of retaining its fluidity when cooled several degrees below its freezing point; and of rising suddenly to this point, when its congelation is promoted by agitation, or by contact with even a warmer thermometer.

4thly, That, like water and other congelable fluids, the vitriolic acid generates cold during its liquefaction, and heat during its congelation; the quantity of which heat and cold, so generated, remains to be determined by future experiments.

5thly, That the acid, by congelation, when the circumstances for distinct crystallization are favourable, assumes a regular crystalline form, a considerable solidity and hardness, and a density much greater than it possessed in a fluid state.

With respect to the first mentioned species of congelation, which is peculiar to the smoking vitriolic acid that is procured from martial vitriol, although I have had no opportunity of seeing it, as all the vitriolic acid, that is used in this country, is obtained by burning sulphur, yet I will beg leave to suggest, that it may be worth the attention of those chemists to whom it occurs, to observe more accurately than has been done, the freezing temperature and the density of the congelable acids; and to examine whether the density of this smoking acid also is connected with the glacial property. It seems further to be deserving of investigation, whether there is not some analogy between the congelation of the smoking oil of vitriol, and the very curious crystallization which Dr. PRIESTLEY observed in a concentrated vitriolic acid, saturated with nitrous acid vapours*; and whether this smoking quality does

* Experiments and Observations relating to various Branches of Natural Philosophy,

does not proceed from some marine or other volatile acid, which may be contained in the martial vitriol, whence the vitriolic acid is obtained.

Philosophy, vol. I. p. 26. and 450. M. CORNETTE has also effected the crystallization of vitriolic acid by distilling it with nitrous acid and charcoal. Memoir, de l'Acad. des Scienc. Paris, pour 1779.